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THE EFFECT OF CONCENTRATION OF ADSORBING SOLIDS ON THE PARTITION COEFFICIENT

DONALD J. O'CONNOR[1] and JOHN P. CONNOLLY[2]

[1]Professor of Civil Engineering, Manhattan College, Bronx, NY 10471 and
[2]Environmental Scientist, U.S. EPA, Environmental Research Laboratory, Gulf Breeze, FL 32561, U.S.A.

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Abstract—The results of a number of laboratory studies are presented to demonstrate an inverse relationship between concentration of adsorbing solids and partition coefficient. Various functional forms which define the relation are developed and correlated with the data. A power-law dependence of partition coefficient on concentration of solids is shown. The significance of this relationship in assessing the fate of hydrophobic pollutants in natural water systems is discussed.

INTRODUCTION

The distribution of heavy metals and organic chemicals in natural water systems is greatly influenced by the interaction between the dissolved and particulate components. This interaction may be due to a number of physio-chemical factors, among which adsorption–desorption is one of the most significant. The nature and concentration of the adsorbing solids determine, in large measure, the rates of these reactions and the resulting equilibrium conditions. The equilibrium condition defines the ratio between the solid-phase and dissolved concentrations, which is referred to as the partition coefficient. This coefficient is a function of various characteristics of the adsorbate and adsorbent. The purpose of this paper is to indicate the effect of the concentration of adsorbing solids on the partition coefficient and to develop various functional forms to define the relationship.

THEORETICAL CONSIDERATIONS

Solids in natural systems consist of inorganic and organic species: the latter may be categorized by detrital and viable components, whereas the former is usually classified by size and chemical composition; clays, silts and sands. Each type of solid has an adsorptive capacity, q_c, that is the ratio of the mass of adsorbate to the unit mass of adsorbent. The total capacity is therefore $q_c m$, in which m equals the concentration of adsorbing solid. The rate of adsorption is assumed to be proportional to the dissolved concentration of the constituent and the difference between the capacity, $q_c m$, and the amount adsorbed, qm. The rate of desorption is proportional to the concentration of the adsorbed mass, qm, thus the kinetic equation may be written:

$$\frac{dc}{dt} = -K_0 mc(q_c - q) + K_2 qm. \tag{1}$$

At equilibrium, equation (1) reduces to

$$q = \frac{q_c c}{\frac{1}{b} + c} \tag{2}$$

in which

$$b = \frac{K_0}{K_2}.$$

The coefficient, b, is related to the energy of adsorption. Equation (2) is the Langmuir isotherm, originally derived for the adsorption of gases by solids.

In natural systems, the adsorptive capacity of the solids, q_c, is invariably an order of magnitude greater than the solid phase concentration, q, and, in many cases, many orders of magnitude greater. Under this condition, equation (2) reduces to

$$q = bq_c c \tag{3}$$

or

$$\frac{q}{c} = bq_c = ¶$$

in which ¶ = partition coefficient.

The partition coefficient is the ratio of the solid phase to the dissolved concentration in the linear portion of the Langmuir isotherm. The magnitude of this coefficient depends on the characteristics of the adsorbate and the adsorbing solids. In general, it varies inversely with the solubility of the adsorbate and directly with the organic and clay fractions of the solids.

Experimental data that do not conform to the Langmuir equation may, in many instances, be fitted by the empirical relation,

$$q = Kc^{1/n} \tag{4}$$

where K and n are constants. Equation (4) is the Freundlich isotherm. For $n = 1$, it is identical to the linear portion of the Langmuir isotherm, the exponent, $1/n$, usually being ≤ 1.

REVIEW OF PREVIOUS WORK

Many laboratory studies on adsorption to soils, sediment and suspended solids have focused on equilibrium behavior, in accordance with the various isotherms described above. The linear relationship has been observed in numerous adsorption studies (e.g. Lambert *et al.*, 1965; Haque *et al.*, 1974; Garnas *et al.*, 1978; Karickhoff *et al.*, 1979), and is the most frequently employed isotherm for describing pesticide adsorption in soils and sediments (Hamaker & Thompson, 1972; Pionke & Chesters, 1973). Hamaker & Thompson (1972), who summarized available data for the Freundlich isotherm of chemicals in soil, have

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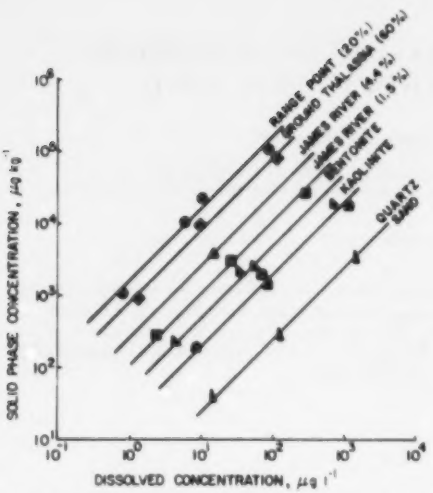

Fig. 1. Adsorption isotherms for Kepone on various solids types. The organic matter content is shown in parentheses.

shown that the exponent $1/n$ varies from about 0.7–1.0. Lotse *et al.* (1968), studying adsorption of lindane to lake sediment, found the data to fit a Freundlich isotherm with the exponent ranging from 0.75 to 0.92. Suzuki *et al.* (1979) found sorption of cadmium to sediment of the Tama River in Japan to follow a Freundlich isotherm with an exponent of about 0.76.

In a series of studies (Reynolds & Gloyna, 1963; Yousef & Gloyna, 1964; Bhagat & Gloyna, 1965), the distributions of radioactive substances in Texas rivers and lakes were investigated. Strontium, cobalt, and ruthenium were among the metals studied. In all cases, the authors noted a decrease in partition coefficient with increasing concentration of sediment, but no corresponding effect as the initial metal concentration was changed. Cox (1970) has reported the partition coefficient for DDT and phytoplankton in a natural environment to be inversely related to phytoplankton density. Using an inverse linear relationship between partition coefficient and concentration of solids, O'Connor & Leahy (1978) modeled the spatial distribution of manganese in Narragansett Bay. The results compared favorably with the observed values of both the dissolved and particulate forms.

The effect of organic matter content and clay content on the extent of adsorption is well-documented (e.g. Lambert *et al.*, 1965; Lambert, 1968; Lotse *et al.*, 1968; Choi & Chen, 1976; Karickhoff *et al.*, 1979). Increased adsorption with increasing clay or organic matter content is due to the high cation exchange capacity and high specific surface area of these materials. Lambert *et al.* (1965), Lambert (1968), and Karickhoff *et al.* (1979) have found the partition coefficient to be linearly related to organic matter content.

Soluble organics and colloidal particles are also important to sorption equilibrium. Using u.v. light absorption to distinguish free and sorbed paraquat, Karickhoff & Brown (1979) found that centrifuging at 20,000 rpm for one hour failed to remove all sorbed paraquat from the water column. In fact, most of the paraquat that remained in the water phase was in the sorbed form. Duursma (1970) found that the addition of soluble amino-acids lowered the sorption of Co and Zn to sediment. Thus, because of the importance of soluble organics and colloidal particles, isotherm studies that use standard phase separation techniques may yield erroneous partitioning values. Centrifugation or filtration is normally used to separate the sediment and water. The compound that remains in the water is assumed to be free and the sorbed compound is computed by difference from the total compound added to the system. Hence, compound sorbed to soluble and colloidal substances not removed by normal phase separation techniques would be incorrectly reported as free compound.

ANALYSIS OF DATA

The primary purpose of this paper is to demonstrate the variation of the partition coefficient with the concentration of suspended solids. It is evident that the nature and characteristics of the adsorbing solids are significant factors in this regard, i.e. the greater capacity of organic matter and the clay fraction to adsorb by contrast to the sands and gravels. It is pertinent to review first the effect of the type of solid as preface to the effect of concentration.

Effect of various types of solids

A typical example is found in data of Garnas *et al.* (1978), which presents the equilibrium between solid-phase concentration and dissolved concentration of Kepone for various types of solids (Fig. 1). The slope of one on the logarithmic coordinates is an indication of the appropriateness of the linear portion of the Langmuir isotherm in the region in which the adsorptive capacity, q_c, is much greater than the solid phase

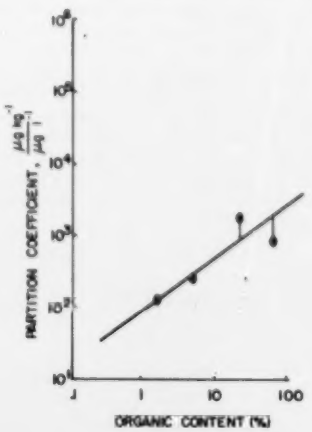

Fig. 2. Partition coefficient as a function of organic matter content.

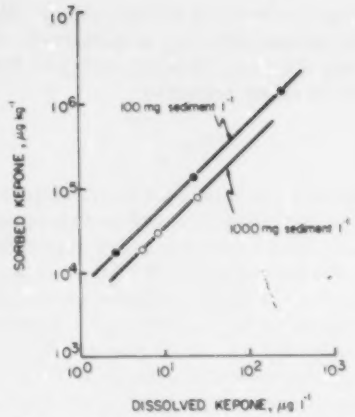

Fig. 3. Kepone Range Point sediment equilibrium isotherms.

concentration, q (equation 3). The influence of the type of adsorbing solids is apparent: the highest partitioning occurring with sediment from Range Point Salt Marsh off Santa Rosa Sound, Florida, which is primarily clay with a high percentage of organic matter.

As the organic content decreases, the partition coefficient decreases, the lowest values being associated with material that is primarily sand. The effect of the organic fraction is presented in Fig. 2. Although each point represents a different sediment, and, therefore, varying fractions and types of clays, the general trend of increasing partitioning with increasing organic content is evident.

Effect of solids concentration

For each solids type shown in Fig. 1 the concentration of the absorbing solids was held constant for the range of Kepone concentration. For a given type of solids, the effect of varying its concentration on the partition coefficient is shown in Fig. 3, which presents the dissolved and solid phase distribution of Kepone for two solid concentrations viz. 100 and 1000 mg l^{-1} (Connolly, unpublished data). Again, the linearity indicates the validity of the Langmuir isotherm and their displacement the difference in partition coefficient viz. 5900 and 3400 due to the varying solids concentration. Similar analyses of data on other substances indicated the same general trend of decreasing partition coefficient with increasing concentration of solids. Although comparable data on all the substances reported in this paper were not available, the fact that the dissolved and solid phase concentrations were relatively low supports the assumption of linearity. The dependence of the partition coefficient of various constituents on the concentration of solids is shown in Fig. 4. Since the purpose of this figure is simply to indicate the spectrum of the general relationships, the lines of correlation are sketched by eye. These data, representative of more extensive sets, include heavy metals, radioactive substances and organic chemicals. The range of solids concentration (10–10,000 mg l^{-1}) covers values for solids in suspension in rivers and estuaries up to values for solids representative of the lower limit encountered in the beds of natural water systems.

The solids effect is most pronounced for constituents characterized by large partitioning, e.g. DDT and radioactive cobalt. For constituents that are represented by intermediate partitioning, the effect of solids concentration is less pronounced and the coefficient approaches a constant value for substances of low partitioning—e.g. strontium.

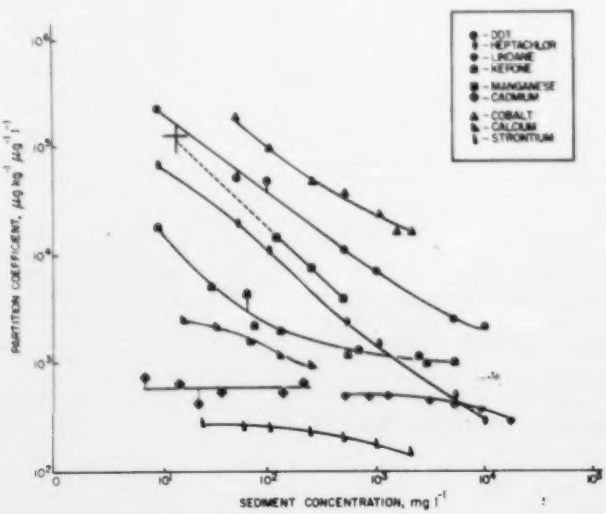

Fig. 4. Partition coefficient as a function of the concentration of solids.

Data correlation

A functional form that correlates the data presented in Fig. 4 is:

$$\P = \P_\infty + \frac{\beta}{m_0 + m^\alpha} \tag{5}$$

in which $\P_\infty$ = limiting partition coefficient at high concentration of solids, m = concentration of solids, and m_0, α, β = empirical coefficients.

The coefficient, β, reflects the relative influence of the solids effect by contrast to the lower limiting value, $\P_\infty$. The coefficient, m_0, allows for the observational fact that, in a few cases, an upper limiting value of the partitioning is approached as the solids concentration decreases. Where a leveling off at low concentration of solids is not evident, the relationship is more appropriately expressed as

$$\P = \P_\infty + \frac{\beta}{m^\alpha}. \tag{6}$$

The linearity of many of the data sets also indicates that the limiting value, $\P_\infty$, is substantially zero, at least over the range of solids reported. Therefore, equation (5) further reduces to:

$$\P = \frac{\beta}{m^\alpha}. \tag{7}$$

As is shown in the following sections, equation (7) fits the majority of the data as well as does equation (6). However, this may be due to the limited range of solids concentrations (10–10,000 mg l^{-1}) for which values of the partition coefficient are available. At high concentrations ($\sim$ 500,000 mg l^{-1}, approximately an average value for bed sediments), a limiting value may be more representative. Equation (6), therefore, is considered to be a more valid, albeit empirical, relationship.

The derived coefficients, determined by least squares, are presented in Table 1. Correlations for organic chemicals are presented in Figs 5 and 6; for radioactive substances, Fig. 7(a); and for heavy

Table 1. Regression of partition coefficients on concentration of solids

Sorbate	System Sorbent	No. of data pts	m_0	β	α	r^2*
Heptachlor	Illite	7	0	1.03×10^5	0.75	0.961[a]
Heptachlor	Kaolinite	7	0	3.98×10^5	0.80	0.997[a]
Heptachlor	Montmorillonite	7	0	7.41×10^4	0.57	0.967[a]
DDT	Illite	7	0	1.80×10^5	0.52	0.993[a]
DDT	Kaolinite	7	0	7.20×10^5	0.83	0.991[a]
DDT	Montmorillonite	7	0	9.41×10^5	0.69	0.986[a]
Dieldrin	Illite	7	0	2.63×10^4	0.67	0.980[a]
Dieldrin	Kaolinite	7	0	8.44×10^4	0.81	0.997[a]
Dieldrin	Montmorillonite	6	0	1.79×10^5	0.92	0.996[a]
PCB	Woodburn soil	5	0	5.50×10^3	0.24	0.954[b]
PCB	Illite	3	0	1.30×10^3	0.19	0.997[b]
Lindane	Lake sediment	7	2.48×10^5	1.14×10^8	1.25	—[c]
Dimilin	Range Point	4	0	7.60×10^3	0.34	0.926[d]
Cobalt	Lake Austin	6	0	3.60×10^5	0.47	0.983[e]
Ruthenium	Lake Austin	6	0	1.80×10^5	0.55	0.964[f]
Strontium	Lake Austin	7	5.82×10^2	1.41×10^5	0.812	—[g]
Cadmium	Digested sludge	3	0	5.70×10^3	0.585	0.996[h]
Manganese	Digested sludge	3	0	9.56×10^5	0.870	0.998[h]
Nickel	Digested sludge	3	0	6.39×10^4	0.546	0.991[h]
Copper	Digested sludge	3	0	1.25×10^6	0.546	0.918[h]
Calcium	River clay	5	0	5.59×10^3	0.31	0.943[i]

Sorbate	System Sorbent	No. of data pts	$\P_\infty$	m_0	β	α	r^2*
Kepone	James River	13	1000	0	2.59×10^5	1.20	0.877[j]
Kepone	Range Point	11	300	0	2.69×10^4	0.34	0.911[j]

* From regression of linearized equation.
[a] Liao (1969).
[b] Haque *et al.* (1974).
[c] Lotse *et al.* (1968).
[d] Garnas (unpublished) USEPA, Gulf Breeze, FL.
[e] Yousef & Gloyna (1964).
[f] Bhagat & Gloyna (1965).
[g] Reynolds & Gloyna (1963).
[h] Rohatgi & Chen (1975).
[i] Garder & Skulberg (1964).
[j] Connolly (unpublished) USEPA, Gulf Breeze, FL.

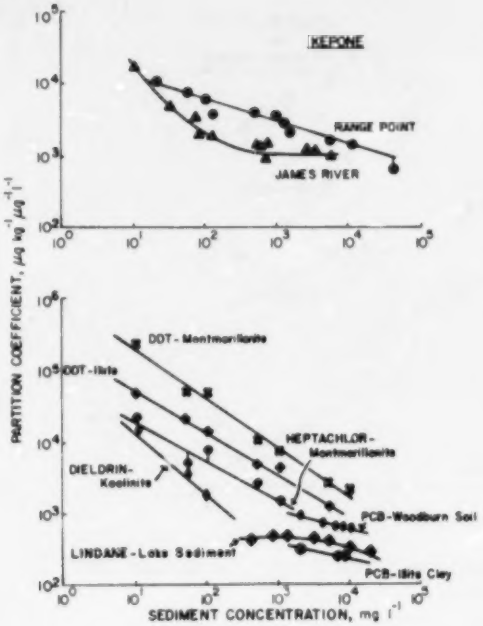

Fig. 5. Correlation of partition coefficient and concentration of solids for organic chemicals.

metals, Fig. 7(b). These graphs and the information in Table 1 show that different compounds adsorbing to the same solids have similar concentration dependences (i.e. similar slopes). This is seen for DDT, heptachlor and dieldrin adsorbing to kaolinite, illite and, with the exception of heptachlor, montmorillonite. Cobalt and ruthenium, adsorbing to Lake Austin sediment have comparable slopes, as do Dimilin and Kepone adsorbing to Range Point sediment and the heavy metals adsorbing to digested sludge. This observation is, in general, not characteristic of single compounds adsorbing to different solids types. For example, the concentration of solids dependence for Kepone adsorbing to James River sediment is much different from that for Kepone adsorbing to Range Point saltmarsh sediment.

It may be inferred from this observation that solids concentration dependent partitioning is a function of the solids, not the compound. A solid–solid interaction may be mediating the adsorption process, resulting in a lowering of the partition coefficient with increasing solids concentration. As noted earlier, the general trend is an increasing level of dependence on concentration of solids with increasing degree of adsorption. Although this may reflect a compound-related effect, it appears that for compounds with the same range of adsorption order the effect of solids-type controls.

SIGNIFICANCE IN NATURAL WATER SYSTEMS

The relationships, presented above, have numerous implications with respect to the distribution of heavy metals and organic chemicals in natural systems. For constituents that achieve equilibrium rapidly with the suspended and bed solids, the application of the principle is particularly significant.

Consider those problem areas, where such constituents have been discharged for some period of time in the past, e.g. Kepone in the James River and PCB in the Hudson River. How much time is required to flush them from the system? The relationship reported here implies that the period required is greater than that for a constant-partition condition. This assessment is based on the following reasoning. The material is now concentrated in the bed. When scoured, the contaminated solids are transported vertically into the flowing waters, diluting the concentration by at least one and, more likely, two or three orders of magnitude. Assuming equilibrium is achieved rapidly, these solids accumulate more of the metal or chemical, due to the increase in partitioning. Upon subsequent settling, the solids re-establish the previous equilibrium by releasing dissolved material to the interstitial waters. The subsequent diffusion of the dissolved material is a relatively slow process,

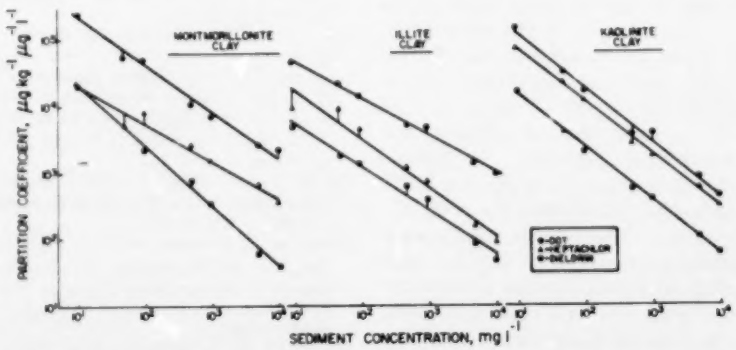

Fig. 6. Correlation of partition coefficient and concentration of solids for chlorinated hydrocarbons on clay.

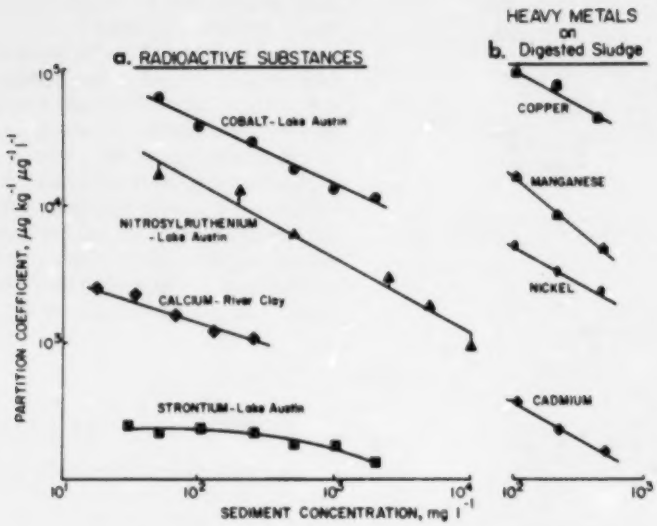

Fig. 7. Correlation of partition coefficient and concentration of solids for (a) radioactive substances, and (b) heavy metals.

thus retaining the constituent in the system longer than if it remained in the flowing waters.

The extent to which conversion between the particulate and dissolved state occurs depends on the rates of adsorption and desorption and on the solids concentrations in the bed and in suspension. For many chemicals and metals, the kinetic rates are relatively rapid (in the order of minutes); for others, the kinetic time scales are of the order of hours and, in some cases, days. The net flux is determined by the kinetic rates and the supply of fresh solids in conjunction with the average residence time in the bed and in the flowing suspension.

CONCLUSION

A functional correlation between the partition coefficient and the concentration of adsorbing solids has been presented as indicating an inverse relationship. Although there is now no fundamental basis for the correlation, a vast amount of experimental data is available to substantiate its validity. In view of the heterogeneity of suspended and bed sediments and variations in experimental conditions, controlled and standardized laboratory evaluation of partition coefficients are recommended. The implications to the distribution and retention of heavy metals and organic chemicals in natural water systems are significant and indicate a tendency to greater retention in these systems than would be the case for a constant partition coefficient. Further work is being directed to a more fundamental understanding of the phenomenon and to the quantitative assessment of this effect in prototype systems.

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